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### (54) Components and catalysts for the polymerization of olefins

Komponenten und Katalysatoren zur Polymerisation von Olefinen

Composants et catalyseur pour la polymérisation d'oléfines

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## Description

The present invention relates to components of catalysts for the polymerization of olefins, to the catalyst obtained therefrom and to the their use in the polymerization of  $\alpha$ -olefins  $\text{CH}_2=\text{CHR}$ , where R is hydrogen or an alkyl cycloalkyl or aryl radical having 1-12 carbon atoms.

Catalyst supported on magnesium dihalide in active form are well-known from the technical literature. They were disclosed the first time in USP 4,298,718 and 4,495,338.

The need for having available high-activity catalysts capable of producing polymers with controlled morphological characteristics is felt in the industrial practice.

Examples of catalysts with controlled morphology are described in USP 3,953,414 and USP 4,399,054. In the latter patent the components are prepared by starting from spherical form adducts of  $\text{MgCl}_2$  with approximately 3 mols of alcohol. Prior to the reaction with  $\text{TiCl}_4$  the alcohol content is decreased down to 2.5-2 mols: in this manner components are obtained which exhibit a porosity, as measured with nitrogen, of from 0.3 to 0.4  $\text{cm}^3/\text{g}$  and an average pore radius comprised between 0.0015 and 0.002  $\mu\text{m}$  (15 and 20 Å).

Catalyst prepared from  $\text{TiCl}_4$  and  $\text{MgCl}_2$  in granular form, by spray-drying an alcohol solution of magnesium chloride and subsequently supporting the titanium compound, are described in patents EP-B-65700 and EP-B-243327. However, the polymer obtained with these catalysts does not exhibit morphological characteristics of interest. In particular the bulk density is not sufficiently high. Furthermore, the activity of the catalyst is rather low.

A method for increasing the activity of these catalysts is described in patent EP-A-281524. The catalysts are prepared by supporting titanium alcoholates onto an  $\text{MgCl}_2$ -ethanol adduct containing from 18 to 25% by weight of ethanol spherulized by spray-drying an ethanol solution thereof, and subsequent chemical treatment with  $\text{Et}_2\text{AlCl}$  or  $\text{Et}_3\text{Al}_2\text{Cl}_3$ . The conditions for preparing the support are critical and have an influence on the morphological stability of the resulting polymer. Polymers in the form of heterogeneous powder are obtained, for example, when supports are used the alcohol content of which is not comprised within the range 18-25%, or when compounds different from  $\text{Et}_2\text{AlCl}$  or  $\text{Et}_3\text{Al}_2\text{Cl}_3$  are used. Furthermore, in order to obtain sufficiently high yields, the Ti content in the solid component is always greater than 8% by weight. EP-A-119963 describes a process for ethylene copolymerization carried out in suspension carried out in the presence of a catalyst component obtained by reacting a titanium halide with an adduct of  $\text{MgCl}_2$  and alcohol. Said adduct is prepared by spray-drying a solution or an emulsion of  $\text{MgCl}_2$  and alcohol, the alcohol being used in large excess with respect to the  $\text{MgCl}_2$ . Spray-drying of solution/emulsion of magnesium dichloride and alcohol is also

described in EP-A-97131.

From European patent application EP-A-395083, high-activity catalysts for olefin polymerization are known which are capable of producing polymers in the form of particles of spheroidal shape endowed with satisfactory morphological properties, in particular high bulk density.

When these catalysts are used for the polymerization of ethylene to produce LLDPE or in general ethylene copolymers with other  $\alpha$ -olefins, the distribution of the comonomer in the polymeric chain is far from optimum.

The solid components of the catalysts described in EP-A-395083 are characterized by a high porosity (as measured by mercury method) and by a distribution of pore radii which is shifted towards pores with a relatively small radius (more than 50% of pores have radius smaller than 0.08  $\mu\text{m}$  (800 Å)).

It has now unexpectedly been found that it is possible to prepare catalysts endowed with a high activity and capable of distributing uniformly the comonomer in the preparation of copolymers of ethylene with  $\alpha$ -olefins and furthermore capable of yielding polymers of spheroidal shape endowed with valuable morphological properties.

The spherical solid components of the present invention comprise, supported on a magnesium dihalide in active form, a titanium compound containing at least one Ti-halogen bond and are characterized by porosity values higher than 1.0  $\text{cm}^3/\text{g}$  and by a pore distribution such that at least 30% of said pores have a radius greater 1  $\mu\text{m}$  (10000 Å), said components being obtainable by reacting:

(a) an adduct having the formula  $\text{MgCl}_2 \cdot m\text{ROH}$ , wherein  $0.1 \leq m \leq 2$  and R is an alkyl, cycloalkyl or aryl radical having 1-12 carbon atoms, said adduct (a) being in turn prepared by thermal dealcoholation of adducts  $\text{MgCl}_2 \cdot p\text{ROH}$ , wherein  $2.5 \leq p \leq 3.5$ ; with  
 (b) a titanium compound in a molar ratio Ti:Mg between 0.3 and 3.

The spherical catalyst components according to the present invention can be obtained by the reaction of said adduct (a) with a titanium compound (b) having the formula  $\text{Ti}(\text{OR})_n \text{X}_{4-n}$ , wherein  $0 \leq n < 2$ , X is halogen and R is an alkyl, cycloalkyl or aryl radical having 1-18 carbon atoms or a -COR moiety, and, optionally, with (c) a reducing compound or a halogenating and reducing compound. Alternatively, the spherical catalyst components according to the present invention can also be obtained by the reaction of said adduct (a) with a titanium compound (b) having the formula  $\text{Ti}(\text{OR})_n \text{X}_{4-n}$ , wherein  $2 \leq n \leq 4$ , X is halogen and R is an alkyl, cycloalkyl or aryl radical having 1-18 carbon atoms or a -COR moiety, and with (c) a halogenating compound, possibly a reducing compound, or a halogenating and reducing compound.

The total porosity is generally comprised between 1.2 and 2.2  $\text{cm}^3/\text{g}$ ; the porosity as referred to pores with

a radius of up to 1 µm (10000 Å) is generally comprised between 0.7 and 1 cm<sup>3</sup>/g.

The specific surface area is higher than 30 m<sup>2</sup>/g, and is generally comprised between 30 and 100 m<sup>2</sup>/g.

The surface characteristic and the porosity are determined by mercury porosimetry according to the method hereinunder described.

The magnesium dihalide in active form comprised in the spherical component of the present invention are characterized by X-ray diffraction spectra wherein the most intense diffraction line appearing in the spectrum of the non-active halide shows a decreased intensity and in said spectra a halo appears, the maximum intensity of which is shifted towards lower angles with respect to the angle of the most intense line.

The particles of the solid component have a spherical or spheroidal morphology with an average diameter comprised between 10 and 150 µm. By "particles with spheroidal shape" those particles are meant in which the ratio of the major axis to the minor axis is equal to, or smaller than 1.5, and preferably smaller than 1.3.

The preferred titanium compounds have formula  $Ti(OR^1)_nX_{y-n}$ , wherein y is the titanium valency, n is comprised between 0 and (y-1), including limits, R<sup>1</sup> is an alkyl radical having from 2 to 8 carbon atoms, in particular n-butyl, iso-butyl, 2-ethylhexyl, n-octyl and phenyl, and X is halogen. When y is 4, n is preferably comprised between 1 and 2.

The adduct of magnesium halide, preferably magnesium dichloride, with alcohols from which the solid components are obtained, are prepared by starting from adducts in the molten state, by emulsifying them in an inert liquid hydrocarbon and then causing the resulting particles to solidify by fast quenching the emulsion. A typical method for preparing these spherulized adducts is described in USP 4,469,648. According to said method, spheroidal adducts are obtained by mixing the molten adduct with at least one other liquid immiscible therewith and chemically inert thereto and in a ratio such that the molten adduct forms the dispersed phase and the liquid mixed therewith forms the continuous phase, subjecting the mixture to turbulent flow to obtain an emulsion, quenching the emulsion to solidify the dispersed phase and collecting the initially molten adduct in the form of solid, spheroidal particles resulting from the quenching.

The solid spheroidal particles obtained in that way generally contain from 2.5 to 3.5 mol of alcohol. These particles are subsequently submitted to thermal treatment at temperature lower than 150 °C, generally comprised between 50 and 130 °C, in order to decrease their alcohol content down to values comprised between 0.1 and 2 mols per mol of magnesium dihalide.

The dealcoholated adducts are then reacted with a titanium compound under suitable conditions. The reaction with titanium compounds results in a further removal of alcohol from the adduct, with magnesium dihalide in active form being obtained, and leads to fixing on the

same a titanium compound having the formula  $Ti(OR)_nX_{y-n}$ , wherein y is the titanium valency, n is a number comprised between 0 and (y-1), including limits, X is halogen, R is an alkyl, cycloalkyl or aryl radical having 1-18 carbon atoms, or a -COR moiety.

Particularly interesting are those compounds having the above said general formula, and in which y is 4, n may range between 1 and 2, X is chlorine and R is selected among n-butyl, isobutyl, 2-ethylhexyl, n-octyl and phenyl.

Typical titanium compounds which may be used in the reaction with said adduct are titanium tetrahalides, in particular  $TiCl_4$ , and titanium trichloroalcoholates, such as, e.g., tri-chlorobutoxy titanium and trichlorophenoxy titanium. In these cases the compound of titanium may be optionally reduced by using reducing agents capable of lowering the titanium valency down to a value of less than 4.

As examples of reducing compounds Al-trialkyl compounds or silicon compounds, such as e.g., polyhydrogensiloxanes, may be cited.

It is also possible to use titanium alcoholates having the formula  $Ti(OR)_4$ . However in this case it must be used a halogenating compound, such as, e.g.,  $SiCl_4$ ,  $TiCl_4$  itself,  $AlCl_3$  and in general compound which are capable of forming titanium haloalcoholates and of reacting with the -OH radicals of the  $MgCl_2$ -alcohol adduct in order to further dealcoholating it, or in order to bring alcohol removal to completion.

Among these compounds also Al-alkyl halides fall, as well as, in general, compounds having halogenating and reducing activity. In these cases the titanium valency is lowered and titanium halo-alcoholates are formed, wherein Ti is at a valency lower than 4.

It is also possible to use complexes of titanium alcoholates with magnesium halides. These complexes can be prepared according to the methods described in USP 4,218,339, the description of which is herein incorporated by reference.

The molar ratio in the reaction between titanium compound and magnesium in the adduct is generally comprised within the range of from 0.3 to 3, and preferably of from 0.5 to 2.

The amount of titanium, expressed as metal Ti, which remains fixed on the carrier may reach, e.g., the value of 15% by weight and preferably is comprised between 1 to 12%.

The titanium compound supported on magnesium halide is fixed in a form which can not be extracted with solvents; it may also be partially present in extractable form.

The components according to the present invention may possibly additionally comprise, in particular when LLDPE with a particularly narrow molecular weight distribution has to be produced, also an electron donor compound, for example a compound selected from ethers, esters, amines and ketones.

In particular said electron donor compound can be

selected from alkyl, cycloalkyl and aryl esters of polycarboxylic acid, such as, e.g., esters of phthalic and maleic acids, in particular n-butyl phthalate, diisobutylphthalate, di-n-octyl phthalate; other useful compounds are those which are described in European patent application EP-A-344755, in particular, 2-methyl-2-isobutyl-1,3-dimethoxypropane; 2-methyl-2-isopropyl-1,3-dimethoxypropane; 2-methyl-2-isopentyl-1,3-dimethoxypropane; 2,2-diisobutyl-1,3-dimethoxypropane.

The electron donor compound is generally present in a molar ratio, with respect to magnesium, of up to 1:2, and preferably comprised between 1:8 and 1:12.

By reacting them with Al-alkyl compounds, in particular Al-trialkyl compounds, the components according to the invention give rise to catalysts which, as already mentioned above, are capable of uniformly distributing the comonomer in the polymer chain, and furthermore make it possible to obtain polymer endowed with particularly interesting morphological characteristics by gas-phase polymerization.

Examples of Al-alkyl compounds usable in catalyst preparation are Al-trialkyl compounds, in particular Al-triethyl, Al-triisobutyl, Al-tri-n-butyl. The ratio of Al:Ti is higher than 1 and generally is comprised between 20 and 800.

As already mentioned the components according to the present invention are particularly useful in the production of ethylene copolymers with  $\alpha$ -olefins  $\text{CH}_2=\text{CHR}$ , in particular linear low density polyethylenes (LLDPE, having a density lower than 0.940) and very low density and ultra low density polyethylene (VLDPE and ULDPE, having a density lower than 0.920 and down to 0.880) consisting of copolymers of ethylene with one or more  $\alpha$ -olefins having from 3 to 8 carbon atoms, in particular butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1.

In said copolymer the content by weight of units derived from ethylene is generally greater than approximately 80%.

The components according to the present invention are advantageously used also in the preparation of high density polyethylenes (HDPE, with density values higher than 0.940) including ethylene homopolymers and copolymers with  $\alpha$ -olefins having from 3 to 14 carbon atoms, and in the preparation of elastomeric ethylene and propylene copolymers and elastomeric terpolymers of ethylene and propylene with minor amounts of a diene, having a content of units derived from ethylene comprised between 30 and 70% by weight.

The polymerization of olefins in the presence of the catalysts obtained from the catalyst components of the present invention can be carried out according to known method, both in the liquid phase and in the gas phase, using for examples the well-known fluidized-bed technique, or under condition in which the polymer is mechanically stirred.

The following examples are supplied for merely illustrative purposes, and should not be construed as being limitative of the invention itself.

The properties indicated are determined according to the following methods:

- 5 - Porosity and specific surface area with nitrogen: these characteristics are determined according to the B.E.T methodology (apparatus used SOROPTOMATIC 1800 by Carlo Erba).
- 10 - Porosity and specific surface area with mercury: these properties are determined by immersing a known amount of sample in a known amount of mercury inside a dilatometer and then gradually increasing mercury pressure by a hydraulic means. The pressure of mercury entering the pores is a function of the diameter of the pores. The measurement is carried out by using a "Porosimeter 2000 Series" porosimeter by Carlo Erba. From the data of mercury volume decrease and of applied pressure, porosity, pore distribution and specific surface area are calculated.
- 15 - Size of the catalyst particles: this value is determined according to a method based on the principle of optical diffraction of monochromatic laser light, using the "Malvern Instr. 2600" apparatus.
- 20 - MIE flow index: ASTM-D 1238
- MIF flow index: ASTM-D 1238
- Flowability: it is the time required by 100 g of polymer to flow through a funnel, the outlet opening thereof having a diameter of 1.25 cm, and the side walls being inclined at 20° to the vertical.
- 25 - Bulk density: DIN-53194
- Morphology and Granulometric distribution of the polymer particles: ASTM-D 1921-63
- Fraction soluble in xylene: determined at 25°C.
- 30 - Comonomer content: percentage by weight, as determined via I.R. spectra.
- Real density: ASTM-D 792.

## EXAMPLES

### PREPARATION OF SPHERICAL SUPPORT ( $\text{MgCl}_2/\text{EtOH ADDUCT}$ )

The adduct of magnesium chloride and alcohol is prepared by following the method as described in example 2 of USP 4,399,054 but operating at 2000 RPM instead of 10000 RPM.

The adduct, containing approximately 3 alcohol mols, has an average size of approximately 60  $\mu\text{m}$ , with a dispersion range of approximately 30-90  $\mu\text{m}$ .

## EXAMPLE 1

### Preparation of the solid component

The spherical support prepared according to the general procedures as described hereinabove, is submitted to a thermal treatment, within the temperature

range 50-150 °C, until a partial dealcoholation is obtained, with the residual alcohol content being of 35% (the molar ratio of ethanol:Mg is of 1.1).

- porosity (B.E.T) 0.017 cm<sup>3</sup>/g (pores < 0.01 µm (100 Å))
- 0.114 cm<sup>3</sup>/g (pores > 0.01 µm (100 Å))
- 0.131 cm<sup>3</sup>/g (total value)
- surface area (B.E.T) 15.8 m<sup>2</sup>/g
- porosity (mercury) 0.43 cm<sup>3</sup>/g (pores < 1 µm (10000 Å))
- 0.775 cm<sup>3</sup>/g (pores > 1 µm (10000 Å))
- 1.205 cm<sup>3</sup>/g (total value)
- surface area (mercury) 15.8 m<sup>2</sup>/g

400 g of the so obtained support are charged in a 6 litres reactor together with 4 litres of anhydrous heptane. While stirring and at room temperature, 568 g of TiCl<sub>4</sub> are gradually added. The reaction mixture is kept at 80 °C for 2 hours, and the solid portion is washed with inert solvent until free TiCl<sub>4</sub> is removed.

After drying, the resulting catalytic component obtained with spherical shape displays the following characteristic:

- total titanium 3.8 % (by weight)
- Mg 17.0 % (by weight)
- Cl 62.7 % (by weight)
- OEt 6.6 % (by weight)
- porosity (B.E.T.) 0.41 cm<sup>3</sup>/g, 50% of which is due to pores with radius > 0.009 µm (90 Å).
- surface area (B.E.T.) 185 m<sup>2</sup>/g
- porosity (mercury) 1.52 cm<sup>3</sup>/g, 46% of which is due to pores with radius > 1 µm (10000 Å). The value of porosity due to pores with radius < 1 µm (10000 Å) is 0.756 cm<sup>3</sup>/g.
- surface area (mercury) 49.4 m<sup>2</sup>/g.

#### Ethylene polymerization (HDPE)

To an autoclave of 4 l, purged with an inert gas, 900 cm<sup>3</sup> of hexane containing 0.45 g of AlEt<sub>3</sub> and 0.012 g of spherical component suspended in 100 cm<sup>3</sup> of the same mixture of AlEt<sub>3</sub>/hexane as previously described, are charged. While stirring the autoclave is heated up to 75 °C and then 3 bars of H<sub>2</sub> and 7 bars of ethylene are fed. The polymerization time is of 3 hours, during which time ethylene pressure is kept constant. After 3 hours the reaction is interrupted by instantaneously venting ethylene and hydrogen, or by poisoning the polymerization reaction with an alcohol or acetone injection. 252 g of polymer having the following characteristics are obtained:

- MIE 0.42 g/10 min
- MIF/MIE 35
- real density 0.962 g/cm<sup>3</sup>
- bulk density (poured) 0.33 g/cm<sup>3</sup>

- flowability 14 sec
- morphology spherical
- P.S.D. > 4000 µm < 0.5 % (by weight)
- 2000-4000 µm 30-40 % (by weight)
- 1000-2000 µm 50-60 % (by weight)
- 500-1000 µm 2-5 % (by weight)
- < 500 µm < 1 % (by weight)

#### Copolymerization of ethylene with 1-butene (LLDPE)

To an autoclave of 4 litres of stainless steel, purged with a N<sub>2</sub> stream for 2 hours at 70 °C, and then washed with anhydrous propane, 0.012 g of solid component and 0.96 g of Al-triethyl mixed with 25 cm<sup>3</sup> of hexane, and 800 g of anhydrous propane are charged. The autoclave is heated up to 75 °C and then 2 bars of H<sub>2</sub> are fed simultaneously with 7 bars of ethylene and 200 g of 1-butene.

During the polymerization ethylene partial pressure is kept constant and 3 g of 1-butene are added per each 30 g of ethylene fed. After three hours the reaction is interrupted by instantaneously venting off the reactants and propane. The amount of polymer produced is 300 g. The polymer characteristics are the following:

- MIE 0.9 g/10 min
- MIF/MIE 31
- real density 0.920 g/cm<sup>3</sup>
- xylene soluble fraction 10 %
- linked butene 6.5 %
- bulk density (poured) 0.40 g/cm<sup>3</sup>
- flowability 15 sec
- morphology spherical
- P.S.D. > 4000 µm < 0.5 % (by weight)
- 2000-4000 µm 30-40 % (by weight)
- 1000-2000 µm 40-60 % (by weight)
- 500-1000 µm 2-4 % (by weight)
- < 500 µm < 1 % (by weight)

#### EXAMPLE 2

The spherical support prepared according to the above described general procedure is submitted to thermal treatment according to the procedure described in Example 1, followed by a further thermal treatment within the temperature range of 100-130 °C, until a value of residual alcohol of about 15% by weight is obtained.

500 g of support obtained in that way are charged to a 5 litres reactor, together with 2.5 litres of anhydrous heptane. 455 g of TiCl<sub>4</sub> are gradually fed while stirring at room temperature. The reaction mixture is then heated up to 100 °C during 60 min and then is kept at that temperature for 2 hours. The liquid phase is discharged and the solid phase is then washed with hexane. 2 litres of hexane are added and then 250 g Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub> diluted in 1000 cm<sup>3</sup> of hexane are fed during a 30-minute time, at room temperature. The mixture is heated at 60 °C for 2 hours. The reaction mixture is washed three times with

2 litres of hexane and then is vacuum dried at 50 °C.

The catalytic component obtained in spherical form displays the following characteristics:

- total titanium 3.5 % (by weight)
- Ti<sup>III</sup> 2.9 % (by weight)
- Mg 20.0 % (by weight)
- Cl 69 % (by weight)
- OEt 3.2 % (by weight)
- porosity (B.E.T.) 0.401 cm<sup>3</sup>/g, 50% of which is due to pores with radius > 0.019 µm (190 Å).
- surface area (B.E.T.) 110 m<sup>2</sup>/g
- porosity (mercury) 1.18 cm<sup>3</sup>/g, 35% of which is due to pores with radius > 1 µm (10000 Å). The value of porosity due to pores with radius < 1 µm (10000 Å) is 0.743 cm<sup>3</sup>/g; within the range 0-1µm (0-10000 Å), 50% of pores have a radius of > 0.072 µm (>720 Å).
- surface area (mercury) 47.4 m<sup>2</sup>/g.

#### Ethylene polymerization (HDPE)

Ethylene polymerization is carried out as described in Example 1 using 0.014 g of spherical solid component. 310 g of polymer are obtained as particles of spherical shape, having the following characteristics:

- MIE 0.186 g/10 min
- MIF/MIE 63
- real density 0.962 g/cm<sup>3</sup>
- bulk density (poured) 0.40 g/cm<sup>3</sup>
- flowability 14 sec
- morphology spherical
- P.S.D. > 4000 µm < 0.5 % (by weight)  
2000-4000 µm 30-40 % (by weight)  
1000-2000 µm 50-60 % (by weight)  
500-1000 µm 2-4 % (by weight)  
< 500 µm < 1 % (by weight)

#### Copolymerization of ethylene with 1-butene (LLDPE)

0.0154 g of spherical solid component are used in order to copolymerized ethylene and 1-butene according to the same procedure as described in Example 1. 340 g of polymer having the following characteristic are obtained:

- MIE 0.47 g/10 min
- MIF/MIE 30
- real density 0.917 g/cm<sup>3</sup>
- xylene soluble fraction 11 %
- linked butene 6.1 %
- bulk density (poured) 0.41 g/cm<sup>3</sup>
- morphology spherical
- P.S.D. > 4000 µm < 0.5 % (by weight)  
2000-4000 µm 30-40 % (by weight)  
1000-2000 µm 50-60 % (by weight)

500-1000 µm	1-3 % (by weight)
< 500 µm	< 1 % (by weight)

#### EXAMPLE 3

- 5
- 10
- 15
- 20
- 25
- 30
- 35
- 40
- 45
- 50
- 55

The spherical support prepared according to the above described general procedure is submitted to thermal treatment according to the procedure described in Example 1, followed by a further thermal treatment within the temperature range of 100-130 °C, until a value of residual alcohol of about 10% by weight is obtained. 2000 g of support obtained in that way are charged into a reactor of 30 litres, together with 20 litres of anhydrous heptane. The suspension is heated up to 45 °C and, while stirring, the following compounds are gradually and sequentially added: 6000 g of Ti(OBu)<sub>4</sub> within a 30-minute time; 2400 g of polymethylhydrogenisiloxane (PMHS), within a 30-minute time; 4260 g of SiCl<sub>4</sub>, within a 60-minute time. The reaction mixture is then heated up to 50 °C during 30 minutes and then is kept at that temperature for 2 hours. The reaction mixture is washed several times in order to remove the excess reactants and the extremely fine powder present by filtering or settling. The spherical component is dried under vacuum at 50 °C and displays the following characteristics:

- total titanium 2.76 % (by weight)
- Ti<sup>III</sup> 1.9 % (by weight)
- Mg 19.2 % (by weight)
- Cl 59.75% (by weight)
- OEt 1.1 % (by weight)
- OBu 9.9 % (by weight)
- porosity (B.E.T.) 0.238 cm<sup>3</sup>/g, 50% of which is due to pores with radius > 0.013 µm (130 Å).
- surface area (B.E.T.) 59.8 m<sup>2</sup>/g
- porosity (mercury) 1.64 cm<sup>3</sup>/g, 52% of which is due to pores with radius > 1 µm (10000 Å). The value of porosity due to pores with radius < 1 µm (10000 Å) is 0.8 cm<sup>3</sup>/g.
- surface area (mercury) 56.6 m<sup>2</sup>/g.

#### Copolymerization of ethylene with 1-butene (LLDPE)

The copolymerization of ethylene and 1-butene according to the same procedure as described in Example 1 yielded a polymer displaying the following characteristics:

- real density 0.9165 g/cm<sup>3</sup>
- xylene soluble fraction 15.2 %
- linked butene 7.9 %
- bulk density (poured) 0.41 g/cm<sup>3</sup>
- morphology spherical
- inherent viscosity 1.8 dl/g (THN; 135 °C)
- yield 18.3 kg/g catalyst.

### Ethylene polymerization (HDPE)

The polymerization of ethylene carried out according to the same procedure as described in Example 1 yielded a polymer constituted by spherical particles having the following characteristics:

- MIE 0.48 g/10 min
- MIF/MIE 33.3
- bulk density (poured) 0.40 g/cm<sup>3</sup>
- flowability 18 sec
- morphology spherical
- P.S.D. > 4000 µm 0 % (by weight)
- 2000-4000 µm 4.4 % (by weight)
- 1000-2000 µm 80 % (by weight)
- 500-1000 µm 13 % (by weight)
- < 500 µm 2.6 % (by weight)
- yield 13 kg/g catalyst

### EXAMPLE 4

The spherical support prepared according to the procedure as described in the general procedure is submitted to thermal treatment as described in example 1, followed by further thermal treatment within the temperature range of 100-130 °C, until a value of residual alcohol of about 10% by weight is obtained.

403 g of support obtained in that way is suspended in 300 cm<sup>3</sup> of anhydrous heptane and is treated for 30 minutes with 230 cm<sup>3</sup> of a solution obtained by mixing at 60 °C 120 cm<sup>3</sup> of Ti(OBu)<sub>4</sub>, 100 cm<sup>3</sup> of heptane and 10 cm<sup>3</sup> of SiCl<sub>4</sub>. The suspension is heated at 45 °C and, within 30-minute time, is treated with 10 cm<sup>3</sup> of polymethylhydrogensiloxane (PMHS), and subsequently within 60-minute time, and still at the same temperature, with 60 cm<sup>3</sup> of SiCl<sub>4</sub>. The solid is decanted off, and a set of washes are carried out according to the same methodology as of Example 3. The solid spherical component is dried at 50 °C and has the following characteristics:

- total titanium 4.6 % (by weight)
- Ti<sup>III</sup> 3.4 % (by weight)
- Mg 16 % (by weight)
- Cl 55.8 % (by weight)
- OEt 5 % (by weight)
- OBu 9.2 % (by weight)
- porosity (mercury) 1.46 cm<sup>3</sup>/g, 52% of which is due to pores with radius > 1 µm (10000 Å). The value of porosity due to pores with radius < 1 µm (10000 Å) is 0.7 cm<sup>3</sup>/g.
- surface area (mercury) 55.1 m<sup>2</sup>/g.

### Ethylene polymerization (HDPE)

The polymerization is carried out in the same way as disclosed in Example 1, except for operating at 85 °C and with a H<sub>2</sub> pressure of 4.7 bars and with an eth-

ylene pressure of 6.3 bars. A product is obtained as spherical particles, which displays the following characteristics:

- 5 - MIE 2.8 g/10 min
- MIF/MIE 29.8
- Bulk density (poured) 0.39 g/cm<sup>3</sup>
- Flowability 17 sec
- Morphology spherical
- 10 - P.S.D. 2000-4000 µm 0.4 % (by weight)
- 1000-2000 µm 50 % (by weight)
- 500-1000 µm 48 % (by weight)
- < 500 µm 1.6 % (by weight)
- yield 10 kg/g catalyst

### EXAMPLE 5

Two solution are prepared separately from each other, inside glass reactors of 5 litres of capacity.

20 Solution (A): 2.4 l of anhydrous heptane are mixed with 1690 g of titanium tetrabutoxyde. Still at room temperature 868 g of AlCl<sub>3</sub> are added. The reaction mixture is heated to 100 °C and after 2 hours at this temperature a solution is obtained which is cooled at room temperature.

25 Solution (B) : to 1710 g of Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub> charged into a flask, 1163 g of AlCl<sub>3</sub> are added. The temperature of the resulting suspension is increased to 70 °C and the resulting mixture is kept stirred 2 hours at that temperature.

30 The resulting solution is cooled down to room temperature.

To a stirred glass reactor of 25 litres equipped with reflux condenser the solution (A) is charged. 1446 g of a spherical support is then fed at room temperature. The support is prepared according to the general methodologies and dealcoholated as described in the preceding examples down to an alcohol content of 9.8% by weight. The suspension is heated to 60 °C and is kept 2 hours at that temperature and then is cooled down to 15 °C.

35 During 2 hours the solution (B) is added while cooling in order to keep the temperature at a constant value. The suspension is heated to 70 °C during a 1.5-hour time and is kept stirred at that temperature for one further hour. After cooling down to 50 °C the resulting suspen-

40 sion of red colour is left standing for 15 minutes. The supernatant liquid phase, which contains also an extremely fine powder material (of non-spherical shape) is removed by siphoning. By means of the same process the residual spherical solid material is repeatedly

45 washed with hexane until any powder fraction and chlorine are removed. The spherical catalyst is then dried under vacuum at 50 °C, for 4 hours. 1200 g of a dry product are obtained, which display the following elemental composition:

- 55 - total titanium 11.9 % (by weight)
- Ti<sup>III</sup> 11.6 % (by weight)
- Mg 12.6 % (by weight)

- Cl 69.6 % (by weight)
- OEt 0.2 % (by weight)
- OBu 0.2 % (by weight)
- Al 1.7 % (by weight)
- porosity (mercury) 1.33 cm<sup>3</sup>/g, 47% of which is due to pores with radius > 1 µm (10000 Å). The value of porosity due to pores with radius < 1 µm (10000 Å) is 0.7 cm<sup>3</sup>/g.
- surface area (mercury) 57.8 m<sup>2</sup>/g.

#### Ethylene polymerization (HDPE)

The polymerization is carried out in the same way as described in Example 1. A product consisting of spherical particles is obtained, which shows the following characteristics:

- MIE 0.18 g/10 min
- MIF/MIE 94.6
- bulk density (poured) 0.42 g/cm<sup>3</sup>
- morphology spherical
- yield 13.5 kg/g

#### Copolymerization of ethylene with 1-butene (LLDPE)

The copolymerization of ethylene and 1-butene according to the same procedure as described in Example 1 yielded a polymer displaying the following characteristics:

- real density 0.908 g/cm<sup>3</sup>
- xylene soluble fraction 23.5 %
- bulk density (poured) 0.45 g/cm<sup>3</sup>
- morphology spherical
- inherent viscosity 1.89 dL/g (THN; 135 °C)
- yield 32.6 kg/g catalyst.

#### EXAMPLE 6

##### Continuous gas-phase polymerization of ethylene and 1-butene to obtain LLDPE

1.19 g/hour of catalyst, prepared as in Example 2, is prepolymerized with ethylene in continuous at 30 °C, with 6.62 g/hour of TEAL being fed.

The resulting prepolymer is continuously fed to a gas-phase fluidized bed reactor, which is at 80 °C and under a 20-bar pressure, and with the following molar composition:

- propane 84.3 %
- ethylene 11.5 %
- 1-butene 1.6 %
- hydrogen 2.1 %

(the balance to 100% is constituted by inert gases).

An average yield of 9.6 Kg/g catalyst is obtained. The resulting polymer displays the following character-

istics:

- MIE 0.87 g/10 min
- MIF/MIE 35.8
- real density 0.921 g/cm<sup>3</sup>
- xylene soluble fraction 13.2%
- linked butene 6.9 %
- bulk density (poured) 0.39 g/cm<sup>3</sup>
- bulk density (tamped) 0.42 g/cm<sup>3</sup>
- flowability 12 sec
- morphology spherical
- P.S.D. > 4000 µm < 0.1 % (by weight)  
2000-4000 µm 53.5 % (by weight)  
1000-2000 µm 42.0 % (by weight)  
500-1000 µm 3.5 % (by weight)  
< 500 µm < 0.9 % (by weight)

#### Claims

20 1. Spherical components of catalysts for olefin polymerization comprising, supported on a magnesium dihalide in active form, a titanium compound containing at least one Ti-halogen bond characterized in that:

- the total porosity is greater than 1.0 cm<sup>3</sup>/g;
- the pore radius distribution is such that at least 30% of the total porosity is due to pore having a radius greater than 1 µm (10000 Å);

25 said components of catalysts being obtainable by reacting:

30 35 (a) an adduct having the formula MgCl<sub>2</sub>·mROH, wherein 0.1≤m≤2 and R is an alkyl, cycloalkyl or aryl radical having 1-12 carbon atoms, said adduct (a) being in turn prepared by thermal dealcoholation of solid adducts MgCl<sub>2</sub>·pROH, wherein 2.5≤p≤3.5;

40 (b) a titanium compound in a molar ratio Ti:Mg between 0.3 and 3.

45 2. Spherical components according to claim 1, characterized in that the total porosity is comprised between 1.2 and 2.2 cm<sup>3</sup>/g.

50 3. Spherical components according to claim 1 characterized in that the porosity due to pores with radius up to 1 µm (10000 Å) is comprised between 0.7 and 1 cm<sup>3</sup>/g.

55 4. Spherical components according to claim 1 characterized in that the surface area is comprised between 30 and 100 m<sup>2</sup>/g.

5. Spherical components according to claim 1 characterized in that the magnesium dihalide in active form

is  $MgCl_2$ .

6. Spherical components according to claim 1 characterized in that an electron donor compound is also present.

7. Spherical components according to claim 1 characterized in that the said titanium compound supported on said magnesium halide in active form has the formula  $Ti(OR^l)_nX_{y-n}$ , in which y is the titanium valency,  $0 \leq n \leq (y-1)$ , X is halogen,  $R^l$  is an alkyl radical having 2-8 carbon atoms.

8. Spherical components according to claim 7 characterized in that y is 4 and n is comprised between 1 and 2.

9. Spherical components according to claim 7 characterized in that X is chlorine.

10. Spherical components according to claim 7 characterized in that  $R^l$  is selected from n-butyl, isobutyl, 2-ethylhexyl, n-octyl, phenyl.

11. Spherical components according to claim 6 characterized in that the electron donor compound is selected from ethers and alkyl, cycloalkyl, aryl esters of polycarboxylic acids.

12. Spherical components according to claim 1 wherein said titanium compound (b) has the formula  $Ti(OR)_nX_{y-n}$ , wherein  $0 \leq n \leq (y-1)$ , y is the titanium valency, X is halogen, R is an alkyl, cycloalkyl or aryl radical having 1-18 carbon atoms or a -COR moiety.

13. Spherical components according to claim 12 characterized in that the compound (b) is a trichloroacoholate of tetravalent titanium.

14. Spherical components according to claim 1 obtainable by reacting said adduct (a) with a titanium compound (b) having the formula  $Ti(OR)_nX_{4-n}$ , wherein  $0 \leq n < 2$ , X is halogen and R is an alkyl, cycloalkyl or aryl radical having 1-18 carbon atoms or a COR moiety, and, optionally, with (c) a reducing compound or a halogenating and reducing compound.

15. Spherical components according to claim 14 characterized in that the compound (b) is  $TiCl_4$  or  $Ti(OR)Cl_3$ .

16. Spherical components according to claim 1 obtainable by reacting said adduct (a) with a titanium compound (b) having the formula  $Ti(OR)_nX_{4-n}$ , wherein  $2 \leq n \leq 4$ , R is an alkyl, cycloalkyl or aryl radical having 1-18 carbon atoms or a -COR moiety, and with (c) a halogenating compound, possibly a re-

5 ducing compound or a halogenating and reducing compound.

17. Spherical components according to claim 16 characterized in that the compound (b) is  $Ti(OR)_4$ .

10 18. Catalysts for the polymerization of olefins  $CH_2=CHR$ , wherein R is hydrogen or an alkyl or cycloalkyl or aryl radical having 1-12 carbon atoms, comprising the reaction product between the spherical components according to claim 1 and an Al-alkyl compound.

15 19. Catalysts according to claim 18 characterized in that the organometallic compound is an Al-trialkyl compound.

20 20. Process for polymerizing ethylene and its mixtures with olefins  $CH_2=CHR$ , wherein R is an alkyl or cycloalkyl or aryl radical having 1-12 carbon atoms, optionally in the presence of minor amount of a diene, comprising the use of catalysts according to claim 18.

25 21. Process according to claim 20 characterized in that the olefin  $CH_2=CHR$  is selected from butene-1, pentene-1, hexene-1, 4-methyl-pentene-1, octene-1.

30 **Patentansprüche**

1. Kugelförmige Katalysatorkomponenten zur Olefinpolymerisation, umfassend, getragen auf einem Magnesiumdihalogenid in aktiver Form, eine Titanverbindung, enthaltend mindestens eine Ti-Halogen-Bindung, dadurch gekennzeichnet, daß:

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- die Gesamtporosität größer als  $1,0 \text{ cm}^3/\text{g}$  ist;
- die Porenradiusverteilung so ist, daß mindestens 30% der Gesamtporosität von Poren mit einem Radius größer als  $1 \mu\text{m}$  ( $10000 \text{ \AA}$ ) stammen,

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wobei die Katalysatorkomponenten erhältlich sind durch Umsetzen:

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- (a) eines Addukts der Formel  $MgCl_2 \cdot mROH$ , worin  $0,1 \leq m \leq 2$  und R einen Alkyl-, Cycloalkyl- oder Arylrest mit 1-12 Kohlenstoffatomen darstellt, wobei das Addukt (a) wiederum durch thermische Entalkoholisierung aus festen Addukten  $MgCl_2 \cdot pROH$ , worin  $2,5 \leq p \leq 3,5$ , erhalten wird;
- (b) einer Titanverbindung in einem Molverhältnis Ti:Mg zwischen 0,3 und 3.

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2. Kugelförmige Komponenten nach Anspruch 1, dadurch gekennzeichnet, daß die Gesamtporosität

zwischen 1,2 und 2,2 cm<sup>3</sup>/g umfaßt wird.

3. Kugelförmige Komponenten nach Anspruch 1, dadurch gekennzeichnet, daß die Porosität von Poren mit einem Radius bis zu 1 µm (10000 Å) zwischen 0,7 und 1 cm<sup>3</sup>/g umfaßt wird.

4. Kugelförmige Komponenten nach Anspruch 1, dadurch gekennzeichnet, daß die Oberfläche zwischen 30 und 100 m<sup>2</sup>/g umfaßt wird.

5. Kugelförmige Komponenten nach Anspruch 1, dadurch gekennzeichnet, daß das Magnesiumdihalogenid in aktiver Form MgCl<sub>2</sub> darstellt.

6. Kugelförmige Komponenten nach Anspruch 1, dadurch gekennzeichnet, daß ebenfalls eine Elektronendonorverbindung vorliegt.

7. Kugelförmige Komponenten nach Anspruch 1, dadurch gekennzeichnet, daß die Titanverbindung, getragen auf dem Magnesiumhalogenid in aktiver Form, die Formel Ti(OR<sup>1</sup>)<sub>n</sub>X<sub>y-n</sub>, worin y die Wertigkeit des Titans darstellt, 0 ≤ n ≤ (y-1), X Halogen darstellt, R<sup>1</sup> einen Alkylrest mit 2-8 Kohlenstoffatomen darstellt, aufweist.

8. Kugelförmige Komponenten nach Anspruch 7, dadurch gekennzeichnet, daß y 4 ist und n zwischen 1 und 2 umfaßt ist.

9. Kugelförmige Komponenten nach Anspruch 7, dadurch gekennzeichnet, daß X Chlor darstellt.

10. Kugelförmige Komponenten nach Anspruch 7, dadurch gekennzeichnet, daß R<sup>1</sup> ausgewählt ist aus n-Butyl, Isobutyl, 2-Ethylhexyl, n-Octyl, Phenyl.

11. Kugelförmige Komponenten nach Anspruch 6, dadurch gekennzeichnet, daß die Elektronendonorverbindung ausgewählt ist aus Ethern und Alkyl-, Cycloalkyl-, Arylestern von Polycarbonsäuren.

12. Kugelförmige Komponenten nach Anspruch 1, worin die Titanverbindung (b) die Formel Ti(OR)<sub>n</sub>X<sub>y-n</sub> aufweist, worin 0 ≤ n ≤ (y-1), y die Wertigkeit des Titans darstellt, X Halogen darstellt, R einen Alkyl-, Cycloalkyl- oder Arylrest mit 1-18 Kohlenstoffatomen oder einen Rest -COR darstellt.

13. Kugelförmige Komponenten nach Anspruch 12, dadurch gekennzeichnet, daß die Verbindung (b) ein Trichloralkoholat von vierwertigem Titan darstellt.

14. Kugelförmige Komponenten nach Anspruch 1, erhältlich durch Umsetzen des Addukts (a) mit einer Titanverbindung (b) der Formel Ti(OR)<sub>n</sub>X<sub>4-n</sub>, worin 0 ≤ n < 2, X Halogen darstellt und R einen Alkyl-,

Cycloalkyl- oder Arylrest mit 1-18 Kohlenstoffatomen oder einen Rest COR darstellt und gegebenenfalls mit (c) einer reduzierenden Verbindung oder einer halogenierenden und reduzierenden Verbindung.

15. Kugelförmige Komponenten nach Anspruch 14, dadurch gekennzeichnet, daß die Verbindung (b) TiCl<sub>4</sub> oder Ti(OR)Cl<sub>3</sub> darstellt.

16. Kugelförmige Komponenten nach Anspruch 1, erhältlich durch Umsetzen des Addukts (a) mit einer Titanverbindung (b) der Formel Ti(OR)<sub>n</sub>X<sub>4-n</sub>, worin 2 ≤ n ≤ 4, R einen Alkyl-, Cycloalkyl- oder Arylrest mit 1-18 Kohlenstoffatomen oder einen Rest -COR darstellt und mit (c) einer halogenierenden Verbindung, gegebenenfalls einer reduzierenden Verbindung oder einer halogenierenden und reduzierenden Verbindung.

17. Kugelförmige Komponenten nach Anspruch 16, dadurch gekennzeichnet, daß die Verbindung (b) Ti(OR)<sub>4</sub> darstellt.

18. Polymerisationskatalysatoren für Olefine CH<sub>2</sub>=CHR, worin R Wasserstoff oder einen Alkyl- oder Cycloalkyl- oder Arylrest mit 1-12 Kohlenstoffatomen darstellt, umfassend das Reaktionsprodukt zwischen den kugelförmigen Komponenten nach Anspruch 1 und einer Al-Alkyl-Verbindung.

19. Katalysatoren nach Anspruch 18, dadurch gekennzeichnet, daß die Organometallverbindung eine Al-Trialkyl-Verbindung darstellt.

20. Verfahren zum Polymerisieren von Ethylen und dessen Gemischen mit Olefinen CH<sub>2</sub>=CHR, worin R einen Alkyl- oder Cycloalkyl- oder Arylrest mit 1-12 Kohlenstoffatomen darstellt, gegebenenfalls in Gegenwart einer geringen Menge eines Diens, umfassend die Verwendung von Katalysatoren nach Anspruch 18.

21. Verfahren nach Anspruch 20, dadurch gekennzeichnet, daß das Olefin CH<sub>2</sub>=CHR ausgewählt ist aus Buten-1, Penten-1, Hexen-1, 4-Methylpenten-1, Octen-1.

## 50 Revendications

1. Constituants sphériques de catalyseurs pour la polymérisation d'oléfines comprenant, supporté sur un dihalogénure de magnésium sous forme active, un dérivé de titane comportant au moins une liaison Ti-halogène caractérisés en ce que :

- la porosité est supérieure à 1,0 cm<sup>3</sup>/g;

- la distribution de rayons de pores est telle qu'au moins 30% de la porosité totale soit due à des pores ayant un rayon supérieur à 1 µm (10 000 Å),

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lesdits composants du catalyseur pouvant être obtenus en faisant réagir :

(a) un adduct répondant à la formule  $MgCl_2 \cdot mROH$ , où  $0,1 \leq m \leq 2$  et R est un radical alkyle, cycloalkyle ou aryle comportant 1 à 12 atomes de carbone, ledit adduct (a) étant lui-même préparé par désalcoolisation thermique des produits d'addition solides  $MgCl_2 \cdot pROH$ , où  $2,5 \leq p \leq 3,5$ .

(b) un dérivé de titane, selon un rapport molaire Ti:Mg compris entre 0,3 et 3.

2. Constituants sphériques selon la revendication 1, caractérisés en ce que la porosité totale est comprise entre 1,2 et 2,2 cm<sup>3</sup>/g.

3. Constituants sphériques selon la revendication 1, caractérisés en ce que la porosité due aux pores d'un rayon atteignant 1 µm (10 000 Å) est comprise entre 0,7 et 1 cm<sup>3</sup>/g.

4. Constituants sphériques selon la revendication 1, caractérisés en ce que la surface spécifique est comprise entre 30 et 100 m<sup>2</sup>/g.

5. Constituants sphériques selon la revendication 1, caractérisé en ce que le dihalogénure de magnésium sous forme active est  $MgCl_2$ .

6. Constituants sphériques selon la revendication 1, caractérisés en ce que un composé donneur d'électrons est également présent.

7. Constituants sphériques selon la revendication 1, caractérisés en ce que ledit dérivé de titane supporté sur ledit halogénure de magnésium sous forme active répond à la formule  $Ti(OR^1)_nX_{y-n}$ , dans laquelle y est la valence du titane,  $0 \leq n \leq (y-1)$ , X est un halogène, R<sup>1</sup> est un radical alkyle comportant 2 à 8 atomes de carbone.

8. Constituants sphériques selon la revendication 7, caractérisés en ce que y est 4 et n est compris entre 1 et 2.

9. Constituants sphériques selon la revendication 7, caractérisés en ce que X est le chlore.

10. Constituants sphériques selon la revendication 7, caractérisés en ce que R<sup>1</sup> est choisi parmi n-butyle, isobutyle, 2-éthylhexyle, n-octyle, phényle.

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11. Constituants sphériques selon la revendication 6, caractérisés en ce que le composé donneur d'électrons est choisi parmi les éthers et les alkyl, cycloalkyl, aryl esters d'acides polycarboxyliques.

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12. Constituants sphériques selon la revendication 1, caractérisés dans lesquels ledit dérivé de titane (b) répond à la formule  $Ti(OR)_nX_{y-n}$ , où  $0 \leq n \leq (y-1)$ , y est la valence du titane, X est un halogène, R est un radical alkyle, cycloalkyle, ou aryle comportant 1 à 18 atomes de carbone ou un résidu -COR.

13. Constituants sphériques selon la revendication 12, caractérisés en ce que le dérivé (b) est un trichloroalcoolate de titane tétravalent.

14. Constituants sphériques selon la revendication 1, obtenus par réaction dudit adduct (a) avec un dérivé de titane (b) répondant à la formule  $Ti(OR)_nX_{4-n}$ , où  $0 \leq n \leq 2$ , X est un halogène et R est un radical alkyle, cycloalkyle ou aryle, comportant 1 à 18 atomes de carbone, ou un résidu COR, et, le cas échéant, avec (c) un composé réducteur ou un composé halogénant et réducteur.

15. Constituants sphériques selon la revendication 14, caractérisés en ce que le dérivé (b) est  $TiCl_4$ , ou  $Ti(OR)Cl_3$ .

16. Constituants sphériques selon la revendication 1, obtenus par la réaction dudit adduct (a) avec un dérivé de titane (b) répondant à la formule  $Ti(OR)_nX_{4-n}$ , où  $2 \leq n \leq 4$ , R est un radical alkyle, cycloalkyle ou aryle comportant 1 à 18 atomes de carbone, ou un résidu -COR et avec (c) un composé halogénant, éventuellement un composé réducteur ou un composé halogénant et réducteur.

17. Constituants sphériques selon la revendication 14, caractérisés en ce que le dérivé (b) est  $Ti(OR)_4$ .

18. Catalyseurs de polymérisation d'oléfines  $CH_2=CHR$ , où R est l'hydrogène ou un radical alkyle, cycloalkyle ou aryle comportant de 1 à 12 atomes de carbone, comprenant le produit de la réaction entre les constituants sphériques selon la revendication 1 et un dérivé alkyl-Al.

19. Catalyseurs selon la revendication 18, caractérisés en ce que le dérivé organométallique est un dérivé trialkyl-Al.

20. Procédé de polymérisation de l'éthylène et de ses mélanges avec des oléfines  $CH_2=CHR$ , où R est un radical alkyle, cycloalkyle ou aryle comportant 1 à 12 atomes de carbone, éventuellement en présence de quantités mineures d'un diène, comprenant l'utilisation de catalyseurs selon la revendication 18.

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21. Procédé selon la revendication 20, caractérisé en ce que l'oléfine  $\text{CH}_2=\text{CHR}$  est choisi parmi butène-1, pentène-1, hexène-1, 4-méthyl-pentène-1 et octène-1.

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